DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 124

CONSTITUTION AND MICROSTRUCTURE OF SILICA BRICK AND CHANGES INVOLVED THROUGH REPEATED BURNINGS AT HIGH TEMPERATURES

BY

HERBERT INSLEY, Laboratory Assistant

and

A. A. KLEIN, Assistant Physicist

Bureau of Standards

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By Herbert Insley and A. A. Klein

CONTENTS

I. INTRODUCTION [1]

The production of the three general classes of refractories manufactured in the United States in 1914 [2] may be roughly divided as follows:

	Per cent
Silica brick	18
Fire clay brick, including bauxite brick	80
Magnesite and chrome brick	2

Of the silica brick produced in the United States approximately 75 per cent is manufactured in Pennsylvania. In the vicinity of Mount Union and Hollidaysburg, Pa., the ganister or quartz rock from which the brick is made occurs on the mountain slopes in floes varying in depth from a few feet to 20 feet. The extensive measures here carry good rock in limited but well-defined areas. Rocks of three other localities are also important. The Baraboo

[1] This paper deals only with the effects on the microstructure of silica brick during the burning. For the effect of different procedures in grinding and burning and the procedure to be followed, considering commercial limitations, to obtain best results the reader is referred to a companion paper on silica refractories, by Mr. D. W. Ross, Bureau of Standards Technologic Paper No. 116.

[2] Seaver, Mineral Industry During 1914, pp. 900–903.

formation in Wisconsin is used in Wisconsin and Illinois. In Alabama a quartzite, probably of Lower Cambrian age, is employed, while in Montana silica brick are manufactured in connection with metallurgical operations from local rocks. The quartzite used in Montana is from the Quadrant formation of Upper Carboniferous age.

Good brick are manufactured from selected high-silica quartzites (containing over 94 per cent SiO_2). After crushing and grinding to size in a wet pan from 2 to 3 per cent of lime is added as milk of lime. After being thoroughly mixed in the wet pan the mass is generally molded by hand in steel molds. The green brick are then transferred to a drier, where the mechancial moisture is removed. After drying they are burned in kilns, usually of the down-draft type, at maximum temperatures, stated by the manufacturers as 2565 to 3000° F (1400 to 1650° C).

During the burning mineralogical changes occur in which minerals of lower density are formed, and this results in a permanent expansion of the brick. If the conditions are such that these changes have progressed but little during the initial burning of the brick, it is quite certain that if these brick be used in metallurgical operations where they are subjected to high temperatures further expansion will take place. Buckling and cracking of restrained silica-brick walls as a result of expansion are by no means unknown and are of serious consequences. It has therefore been the aim of the silica-brick manufacturer to "take out the expansion," as he terms it.

II. LITERATURE

The various modifications of silica and their thermal relations have interested a number of investigators in the last decade. They have attacked this problem both in the interest of pure science and from its practical application to silica brick. Grum Grzimailo,[3] in his study on the refractoriness of silica brick, found tridymite present, and attributed the expansion to its formation. He stated that a brick which had received sufficient heat treatment to change all the silica to tridymite would suffer no further permanent expansion on heating.

Of interest is the work of Holmquist.[4] He found that the burning of silica brick resulted in the formation of quartz, glassy slag,

[3] Grum Grzimailo, Die Feuerfestigkeit der Dinassteine, Stahl und Eisen, **31**, pt. 1, pp. 224–226; 1911.

[4] Holmquist, Über die Bildung von Tridymit und Cristobalit in Quarz-Ziegeln, Sonderabdruck aus geologiska Föreningens I Stockholm Förhandlingar; April, 1911.

and tridymite. Tridymite was noted mainly in the powdery, fairly porous groundmass, and its formation began in the vicinity of what were originally small segregations of lime. The large quartz grains changed but slowly, first, into what he called a glass, since he found it to be completely isotropic, and then into tridymite when the quartz content became low. These changes did not, however, follow in regular sequence, so that in a small piece of silica brick he found the three modifications quartz, glass, and tridymite. In silica brick which had begun to melt in a Martin furnace he observed cristobalite in irregular, rounded crystals, sometimes assuming an octahedral habit. These were weakly birefringent and showed complex twinning. They lay embedded in a light-yellow to brownish-black, almost opaque glass.

H. Schulze and Alfred Stelzner,[5] as early as 1881, found tridymite and zinc spinel in the mass of a muffle used in a furnace which was employed in the distillation of zinc. The tridymite occurred as small aggregates of tabular crystals and twins in a yellow glass. A few grains of quartz remained, which were badly fractured.

Rieke and Endell[6] have investigated extensively the constitution of silica brick and the volume changes attendant on the burning. They also examined the rate and products of devitrification of quartz glass. They noted that after the first burn cristobalite comprised about two-thirds, while after 10 burns the groundmass was converted in a large degree to tridymite. After 50 burns the brick was composed almost entirely of tridymite. They therefore concluded that the first transformation of the quartz was to cristobalite, and that after repeated burnings the latter inverted to tridymite. The melting point of cristobalite, as determined by them in an iridium resistance furnace, was placed at $1685 \pm 10°$ C. These authors found that cristobalite was the devitrification product of quartz glass. Their table representing the amount of devitrification compared with temperatures and time of heating is as follows:

---

[5] Schulze and Stelzner, Neues Jahrbuch für Mineralogie, Geologie und Palentologie, **1**, p. 145: 1881.

[6] Endell und Rieke, Über die Umwandlungen des Kieselsäureanhydrids bei höheren Temperaturen, Zeitschrift fur Anorganische Chemie., **79**, pp. 239–259: 1913.

Endell und Rieke, Silikat Zeitschrift, **1**, p. 6: 1913.

Endell, Über die Konstitution der Dinassteine, Stahl und Eisen, **32**, pt. 1, pp. 392–397.

Endell, Über Silika Quarzite, Stahl und Eisen, **33**, pt. 2, pp. 1770–1775, 1855: 1913.

TABLE 1

	1200°	1300°	1400°	1500°	1600°
	Per cent	Per cent	Per cent	Per cent	Per cent
½ hour	.....	.....	5	34	60
1 hour	0	2	17	50	90
2 hours	.....	5	25	100	.....
4 hours	0	10	.....	.....	.....

In this country the Geophysical Laboratory has taken up the question of the various forms of silica and their stability relations. Their work on silica culminated in a publication by Fenner [7] on the stability relations of the silica minerals. From a scientific standpoint this is the most comprehensive work yet published on this subject. It has a direct bearing on the question of the constitution of silica brick. Disregarding chalcedony, Fenner found seven distinct modifications of silica: α and β, quartz; α, β_1, and β_2, tridymite; α and β, cristobalite. Fenner distinguished two types of silica inversion, both enantiotropic. "One is distinguished by a small energy change, small change of optical and crystallographic properties, and readiness of reaction; the other by a much greater change of optical and crystallographic properties, by sluggishness of reaction, and by energy changes, probably of considerable amount. The evidence which has been presented suggests an explanation of the differences. It points to the conclusion that in inversions of the first type the process is simply a small rearrangement of the molecules within the crystal structure; in those of the second type the change is much more radical and involves the destruction of one sort of molecular species and the formation of another." The inversion of quartz to tridymite and of tridymite to cristobalite was found to be greatly hastened by the addition of a flux. Sodium tungstate proved to be the most satisfactory flux. The inversion temperatures at atmospheric pressure were:

$$870 \pm 10^\circ \text{ quartz} \rightleftharpoons \text{tridymite}$$
$$1470 \pm 10^\circ \text{ tridymite} \rightleftharpoons \text{cristobalite}$$

The process of transformation of one form of silica into another in many cases followed Ostwald's Law of Successive Reactions: "In all reactions the most stable state is not straightway reached, but the next less stable, or that state which is the least stable of all possible states." For example, Fenner found that, by heating amorphous silica at 1300 or 1400°, cristobalite alone was obtained,

[7] Fenner: American Journal of Science, ser. 4, 36, pp. 331-384: 1913.

although tridymite is the stable modification for those temperatures. Similarly ground quartz heated without a flux at high temperatures, but below 1470° changed to cristobalite, and not to tridymite. For the specific gravities of tridymite and cristobalite the following values were obtained: Tridymite at 27° referred to water at 27° specific gravity = 2.270; cristobalite under the same conditions, specific gravity = 2.333. New determinations of the α to β inversions of the several species gave the following values:

α quartz $\rightarrow \beta$ quartz, 575° C
β quartz $\rightarrow \alpha$ quartz, 570° C
α tridymite $\rightarrow \beta_1$ tridymite 117° C
β_1 tridymite $\rightarrow \beta_2$ tridymite, 163° C

Reversions on cooling not very sharp.

α cristobalite $\rightarrow \beta$ cristobalite, 274.6 to 219.7°, depending upon previous heat treatment.
β cristobalite $\rightarrow \alpha$ cristobalite 240.5 to 198.1° depending upon previous heat treatment.

The melting point of cristobalite was found to be close to 1625°, a value decidedly below that given by Endell and Rieke. More recent investigations indicate a considerably higher melting point of $1710 \pm 10°$ for cristobalite and $1670 \pm 10°$ for tridymite.[8]

Klein has contributed petrographic observations in a publication by Seaver [9] dealing with the manufacture and tests of silica brick and the physical changes involved in their initial burning and reburning at high temperatures. The temperature of burning and reburning (about 1540° C) was higher than the tridymite-cristobalite inversion point, and it was, therefore, not surprising that cristobalite was the only inversion product noted. The petrographical results may be tabulated as follows:

TABLE 2

	Cristobalite	Quartz and silicates
First burn	77.35	22.65
Second burn	82.37	17.13
Third burn	83.98	16.02

Day, Sosman, and Hostetter [10] plotted a curve for the change in volume of 1 kilogram in cubic centimeters against the burning

[8] Ferguson and Merwin, Am. Jour. Sci.; August, 1918.
[9] Seaver, Manufacture and Tests of Silica Brick for the By-Product Coke Oven, Transactions of the Amer. Inst. of Min. Eng., 53, p. 125; 1916.
[10] Day, Sosman, and Hostetter, Determination of Mineral and Rock Densities at High Temperatures, Amer. Jour. of Sci., ser. 4, 37, pp. 1–39; 1914.

temperature. Their curve shows particularly the break due to the inversion of α to β quartz and the great increase in volume starting about 1250° C due to the formation of cristobalite.

H. Le Chatelier, studying silica expansion,[11] determined the curves representing dilatation in 100 mm against heating temperature up to 1000° C for quartz, tridymite, cristobalite, and silica glass. The breaks in the curves correspond very faithfully to the inversion points determined by other methods.

McDowell [12] made a number of microscopic analyses, together with crushing, cross-breaking, density, porosity, and spalling tests on silica brick. He also collected data on specific gravities and permanent expansion of bricks of various burns. He concludes that the larger part of the quartz is transformed into cristobalite at the first burn and that the remaining quartz is very slowly transformed on repeated burning; that "the cristobalite at first slowly, and later more rapidly, inverts to tridymite." Although he finds that tridymite forms nearly as rapidly in the brick of coarse or regular grind as it does in the brick of finer grind, nevertheless the tridymite always seems to form first in the finer-grained groundmass. He explains this by the relatively higher concentration of lime in the groundmass. All the 2 per cent of lime added during the mixing must necessarily be found in the groundmass, since it can not penetrate the more or less solid phenocrysts.

III. PRESENT INVESTIGATION

From a review of the literature on this subject one is impressed with the close relation between the constitution of silica brick and its desirability as a refractory material. It is easy to conceive of a brick being burned and acquiring considerable strength without much inversion of the original quartz. Such a brick might apparently be of the highest quality, although, as previous work has shown and as this report will show, it is liable to excessive expansion, which might lead to disastrous effects in metallurgical construction. Other investigators have also shown that the microstructure and the mineral composition of a brick affect to a certain extent its crushing strength, cross-breaking strength, and spalling tendency. For these reasons it was decided to make a microscopic petrographic study of American silica brick to determine, first, the original constitution; and, second, the com-

[11] Le Chatelier, La Silice et les Silicates, pp. 125, 226.
[12] McDowell, A Study of the Silica Refractories, Bull. 119, Amer. Inst. of Min. Eng.; November, 1916.

ponent or components of silica brick, stable under conditions of repeated burning, such as it would undergo in the industries.

To this end letters were sent to various manufacturers requesting data on the raw material and the burning conditions for their silica brick, as well as samples of silica raw material, of green brick, of regular burned brick, and of brick used in kilns, ovens, etc., where they would receive repeated burnings at high temperatures. A willingness to cooperate was manifested in practically every case.

IV. METHODS OF INVESTIGATION

Inasmuch as the problem was one involving the determination of the constitutents in as nearly a quantitative manner as possible, and inasmuch as the microstructure was also thought to be important, the petrographic work involved the study of immersed grains and thin sections. For the quantitative determination of the relative amounts of different minerals present the brick was ground in an agate mortar to pass through a 200-mesh screen. The three principal minerals in silica brick, quartz, tridymite, and cristobalite, can be most easily distinguished by their different indices of refraction. By immersing the powdered brick grains in a liquid of known index of refraction the minerals having indices higher than the index of the liquid could easily be distinguished from those having indices lower than the index of the liquid.

The method used in the determination of the amounts of the several constituents was very similar to that used by Klein [13] in determining the quartz content of porcelains and feldspars. The microscope was attached to a camera of the type usually used for photomicrographic work. A plane-glass plate to which tracing paper was fastened was used instead of the regular ground glass plate. The lens system and the camera length used gave a magnification of about 400 diameters. The image of the field was obtained on the paper and the grains traced. The grains on the tracing paper were cut out. Those which represented grains having an index of refraction higher than that of the liquid were weighted separately from those which represented grains with an index of refraction lower than that of the liquid, and the relative percentages of the two were calculated. While quartz has an average index of refraction quite different from the average indices of cristobalite and tridymite, the last two have average refractive indices which differ from each other by only 0.014. It

[13] Klein, The Constitution and Microstructure of Porcelain, Transactions of the American Ceramic Society, 18, p. 899.

would be very difficult to use a liquid with an index of refraction differing from those of tridymite and cristobalite by 0.007, owing to the faintness of the Becke line and the Schroeder van der Kolk phenomenon. Furthermore, the dispersion effect would necessitate the use of monochromatic light. Where a large number of determinations had to be made, as in this case, it was necessary to devise a more satisfactory method. The following method was therefore worked out: The powdered brick grains were immersed in a liquid with an index of refraction of 1.51. Here the percentage of quartz was determined and the combined percentage of cristobalite and tridymite. Then the grains were immersed in a liquid with an index of refraction equal to the mean index of either tridymite or cristobalite, depending on whether tridymite was present in excess of cristobalite or vice versa. If tridymite were in excess, the liquid employed would be one with the mean refractive index of tridymite, causing tridymite to disappear in the field. The distinction would then be made between cristobalite with a mean index slightly higher than that of the liquid and quartz, with a mean index considerably higher than that of the liquid. If the reverse were the case and a liquid with an index of 1.485 were used, then the cristobalite would disappear, and the distinction would be made between the tridymite with a slightly lower mean index and the quartz with a considerably higher mean index.

For instance, suppose that the value obtained for quartz was 30 per cent and for cristobalite and tridymite 70 per cent. If an examination of the material proved that the cristobalite was in excess of the tridymite, then the material would be immersed in a liquid of index 1.485 to remove the cristobalite. Suppose the quartz and tridymite determinations gave values of 60 per cent and 40 per cent, respectively. Then the actual amount of tridymite would be determined by the proportion $60 : 40 = 30$ per cent (the actual amount of quartz present): X and $X = 20$ per cent. The values therefore would be as follows: Thirty per cent quartz, 20 per cent tridymite, and 50 per cent cristobalite. In the determinations five analyses were made and the average taken to determine the amount of quartz present and five other analyses to determine the amount of tridymite or cristobalite. Errors may be present due to poor sampling, slight change in index of refraction of the liquid through change in temperature, and inaccuracy in cutting out and weighing the tracing paper. An error of 5 per cent is considered possible. As the glass and the calcium metasilicate

present in the brick have higher indices than quartz, they are not distinguished from quartz in the analyses and are included with it under the heading quartz and silicates. The silicates are, however, only present in small amounts.

There are only four minerals that can ordinarily be identified in the microscopic examination of silica brick: Quartz, tridymite, cristobalite, and pseudowollastonite, the α modification of calcium metasilicate, $CaO.SiO_2$.

The optical properties of quartz are well known.[14] Quartz has fairly low indices of refraction $\omega = 1.544$, $\epsilon = 1.553$ for yellow light. Its double refraction is low, about 0.009, giving a gray to yellow interference color of the first order, with crossed nicols for sections of the usual thickness (0.02 to 0.04 mm). The optical character is positive and the interference figure uniaxial. The crystal system is hexagonal. There are two forms of quartz: α quartz which is stable below 575° C, and β quartz which is stable above 575° C. With a change in temperature beyond the inversion point the change from one form to the other takes place readily.

Tridymite shows three modifications: α tridymite stable below 117° C; β_1 tridymite, stable between 117 and 163°; and β_2 tridymite, stable above 163° C. α tridymite is probably orthorhombic, while the β forms are hexagonal. The orthorhombic form is the one always seen under the microscope. The indices of refraction are low; α and β are almost the same, about 1.469, while γ is about 1.473. The double refraction is very low, about 0.004, giving a faint gray interference color with crossed nicols in the ordinary thin sections. Optical character positive; extinction parallel; optic axial angle fairly large. Twinning is very common, the most usual forms seen in silica brick being the wedge-shaped twins. Sections of interpenetration twins are also common. The hexagonal plates and laths noted by Fenner are much rarer than the twinned forms in silica brick.

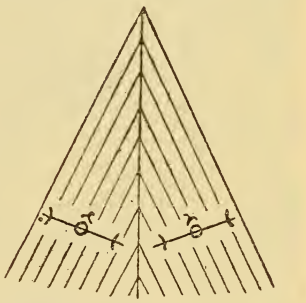

Diagram of wedge-shaped twin

Cristobalite shows two modifications: α cristobalite inverts to β cristobalite at 275 to 220° C, while the inversion from β to α cristobalite takes place at from 240 to 198° C. The variations

[14] For a discussion of the optical properties of the silica minerals see Fenner, The Stability Relations of the Silica Minerals, Amer. Jour. of Sci., ser. 4, 36, pp. 331–383.

in the inversion points depend upon the previous heat treatment of the mineral.[15] β cristobalite is isotropic while α cristobalite, the form stable at ordinary temperature, is probably tetragonal. The crystals in silica brick are so small that the crystal faces are indistinct and the individuals usually appear as short needles. The mean index of refraction is about 1.485. While the double refraction is probably but slightly lower than that of tridymite, the individual crystals are so small that the double refraction is not apparent and the mineral appears to be isotropic. Usually the double refraction can only be seen with the aid of the sensitive tint plate.

Pseudowollastonite[16] is the α form of calcium metasilicate ($CaO.SiO_2$). It crystallizes at temperatures above 1190° C, while wollastonite, the β form, crystallizes at temperatures below 1190° C. The α form rarely inverts to the β form on cooling. Pseudowollastonite occurs in silica brick in small amounts and in very minute irregular grains. Because of the minuteness of the grains, the optical properties are hard to distinguish. The mean index of refraction lies between 1.62 and 1.65; double refraction high; optical axial angle variable, but usually rather small; optically positive.

In a large number of silica-brick samples, particularly those having more than one burn, the presence of a glass was noted. The glass seems to be variable in composition, and is probably caused by the fluxing action of the lime added in the making of the brick, together with the iron oxides and the other impurities present in the original quartzites. In some bricks the color of the glass is a deep yellow, while in others it is practically colorless. Its index of refraction probably varies considerably in different bricks, but it is much higher than that of quartz. The glass usually occurs surrounding or between the tridymite crystals.

V. ANALYSES AND EXAMINATION

In presenting the discussion of the various bricks it was thought that a geographical division was the most rational one to make for a basis of comparison, since, as in the case of Pennsylvania, most of the manufacturers from the same region were using stone of the same geological formation as a source of the raw material.

[15] Fenner, American Journal of Science, ser. 4, 36, pp. 331–383.

[16] Allen, White, and Wright, Wollastonite and Pseudowollastonite, Polymorphic Forms of Calcium Metasilicate, American Journal of Science, ser. 4, 21, pp. 89–108; 1906.

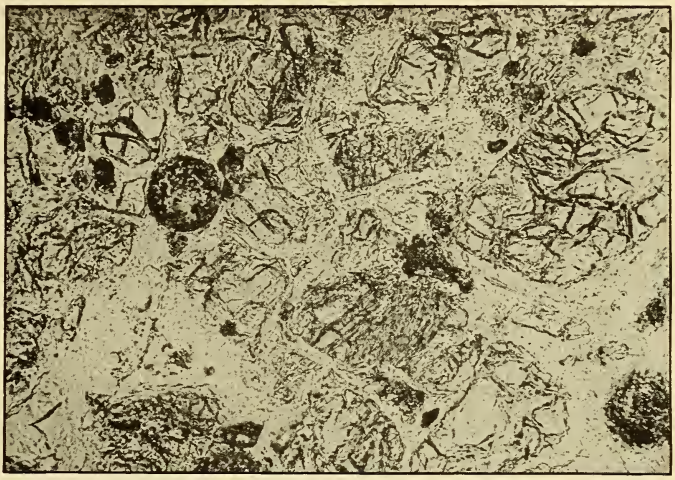

FIG. 1.—*Phenocrysts in the regular one-burn brick of manufacturer (a) in ordinary light*

The dark lines represent cracks formed by the shattering of the quartz grains. Magnification= 160 diameters

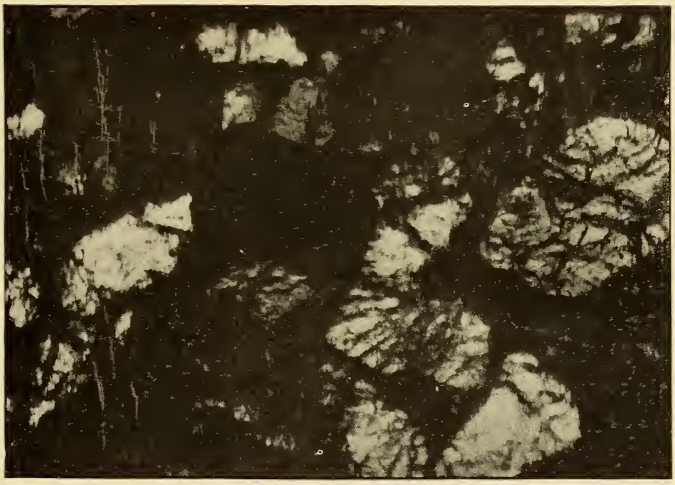

FIG. 2.—*Same as Fig. 1, but taken with plane polarized light and crossed nicols*

The doubly refracting areas are mainly quartz. Some small tridymite crystals appear in the groundmass. The isotropic areas are cristobalite. Magnification= 160 diameters

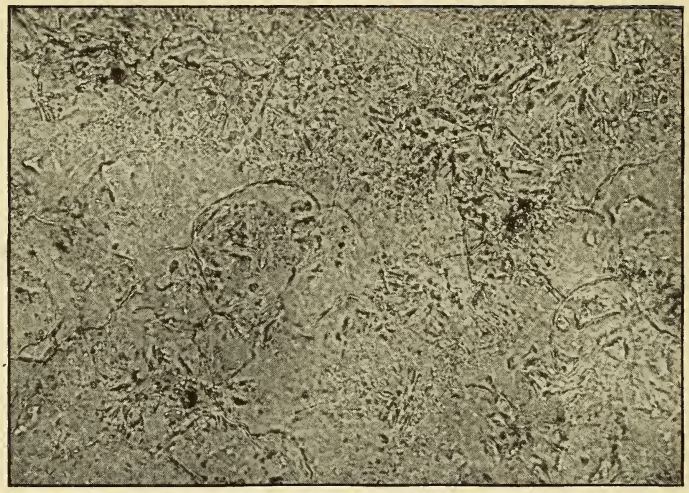

FIG. 3.—*Groundmass of regular one-burn brick of manufacturer (a) in ordinary light*

Magnification=260 diameters

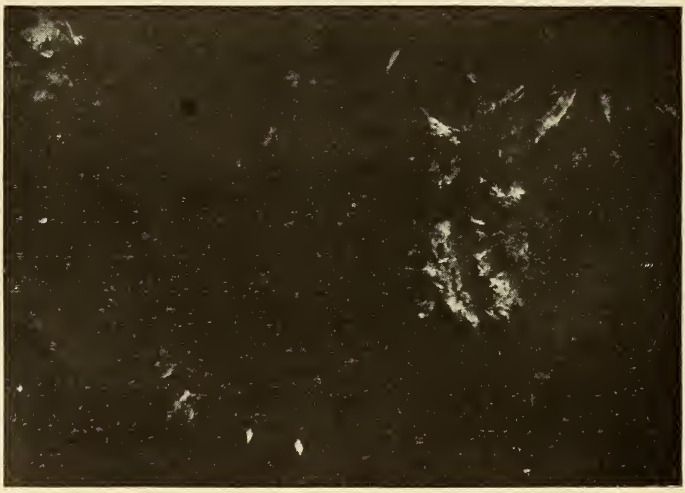

FIG. 4.—*Same as Fig. 3, but taken with plane polarized light and crossed nicols*

The doubly refracting areas are mainly small tridymite crystals; the dark areas are cristobalite and glass. Magnification=260 diameters

1. PENNSYLVANIA BRICK

MANUFACTURER (a)

(1) *Quartzite.*—Megascopically the Medina quartzite used by this company is a typical gray quartzite often showing limonitic discoloration. The chemical analysis is given in Table 3. The quartzite is hard, compact, and homogeneous. The individual sand grains are invisible without the use of a lens. The rock is traversed by sericitic and limonitic veins. Microscopically the siliceous cementing material of the rock is found to be entirely crystallized and to conform crystallographically and optically to the orientation of the original sand grains, so that in most cases it is difficult to distinguish primary from secondary quartz. The crystals are anhedral to subhedral, sometimes showing a rough hexagonal outline. No distinct porphyritic-like structure is visible. The largest crystal observed is 0.85 mm across (Fig. 9). Only very small amounts of accessory minerals, such as limonite, sericite, kaolin, or biotite, are present.

(2) *Regular Brick, One Burn.*—The exact data as to the procedure employed in burning this brick are not known, but the maximum temperature reached in burning was about 1400° C. The brick is composed of dull white areas, which might be called phenocrysts and which are the remains of the large fragments of the original ground quartzite, and a yellowish, granular groundmass which shows a slight vitreous luster. In spots where there is a segregation of ferruginous material the iron has fluxed, forming deeply colored spots varying from red to black. The chemical analysis is given in Table 4. Microscopically the phenocrysts usually consist of shattered quartz grains, all the fragments of which extinguish in the same position. The phenocrysts are surrounded by rims of cristobalite (Figs. 1 and 2), and the interstices of the broken grains are filled with this mineral. No tridymite is found in the phenocrysts. Most of the groundmass consists of cristobalite, with large amounts of tridymite (Figs. 3 and 4). The tridymite crystals are very small, the high index glass usually being found in connection with them. Pseudowollastonite is also present in the groundmass in small quantities. The mineralogical composition of this brick is given in Table 5.

(3) *Brick, Reburned Six Times.*—This brick had six burns each time under approximately the same conditions as brick (2) of this company. This brick is denser and more evenly colored than the regular brick. The luster is decidedly more vitreous, particularly

in the phenocrysts which lack the dull, fractured appearance of the regular brick. The brick consists in large part of tridymite, although tridymite is not present in most of the phenocrysts. Usually the quartz of the phenocrysts has been transformed entirely to cristobalite. Occasionally corroded quartz remnants are seen in phenocrysts. The groundmass consists almost wholly of tridymite, with small quantities of glass. Very little, if any, pseudowollastonite is present. The mineralogical composition is given in Table 5.

(4) *Brick Used in a Magnesite Kiln and Reburned 10 or More Times.*—Information as to the burning conditions of this brick was not available. The brick possesses a deeper-yellow color than the regular and six-burn bricks and appears to be more vitreous. The phenocrysts, while still lighter colored than the groundmass, tend toward a faint yellowish color. The luster is vitreous and lacks the dull, sugary, fractured appearance noted in the regular brick. The brick is composed almost wholly of tridymite, very little quartz or cristobalite being present. A rather large amount of glass, however, is seen. The phenocrysts are formed of small tridymite crystals (Figs. 5 and 6), whereas the tridymite crystals of the groundmass are large and well formed, much larger than those of bricks (2) and (3). In this brick the tridymites are usually well-developed, wedge-shaped twins, the largest individual being about 0.2 mm long (Figs. 7 and 8). The mineralogical composition is given in Table 5.

(5) *Brick Used in Crown of Clay Kiln.*—Concerning the brick the company writes: "The sample from the crown of a clay kiln has been in service for a number of years and has had many burnings at different temperatures, depending upon the grade of material burned in the kiln. At times this specimen may have been subjected to temperatures corresponding to cone 15 (about 1435° C), while at other times it may have been burned at a temperature of less than cone 10 (1300° C)." Both megascopically and microscopically the brick had practically the same appearance as the magnesite kiln brick. The mineralogical composition is given in Table 5.

MANUFACTURER (b)

(1) *Quartzite.*—According to the company's communication, this sample was taken from Blair County, Pa. It is, no doubt, of Medina age. It resembles very closely the quartzite used by manufacturer (*a*), except that it is possibly a little more equigranular.

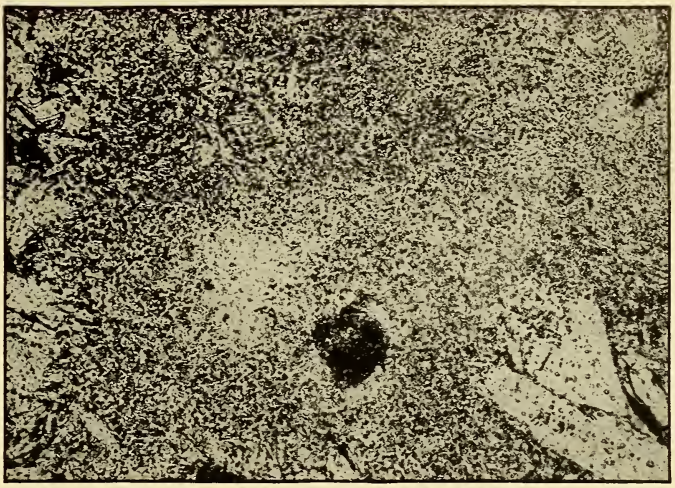

FIG. 5.—*Phenocryst of brick (4) of manufacturer (a) as taken in ordinary light, showing the large number of small tridymite crystals composing it*

Magnification= 160 diameters

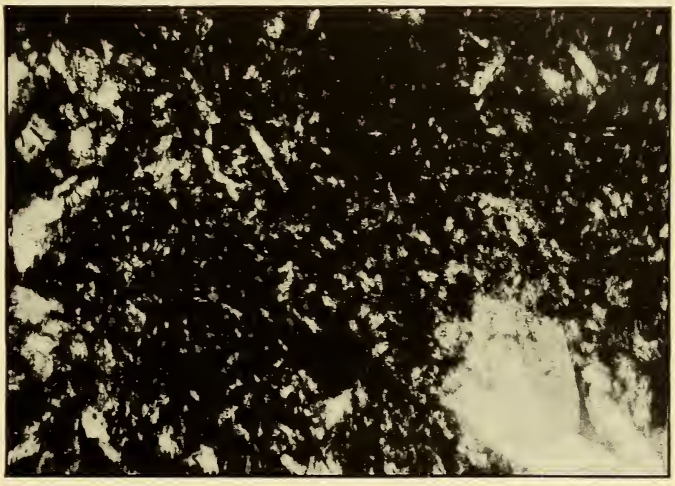

FIG. 6.—*Same as Fig. 5, but taken with plane polarized light and crossed nicols*

On the left-hand margin and in the lower right-hand corner are seen large wedge-shaped twins and laths of tridymite formed in the groundmass of the brick. Magnification= 160 diameters

FIG. 7.—*Groundmass of brick (4) of manufacturer (a), showing in ordinary light large tridymite crystals*

Magnification= 160 diameters

FIG. 8.—*Same as Fig. 7, but taken with plane polarized light and crossed nicols*

Note the wedge-shaped twins and lath development and compare with Figs. 5 and 6, which are the same magnification (160 diameters)

(2) *Regular Brick, One Burn.*—Concerning this brick the company writes: "The temperature at which these bricks were burned will approximate 3000° F (1649° C), and they are held at this temperature for 48 hours; the total duration of burn was nine days." The brick appears tough and nonfriable. The exterior is colored light yellow with reddish-brown to black slag spots. The fracture surfaces are irregular. The chemical analysis is given in Table 4. The phenocrysts are composed of shattered quartz grains, with cristobalite filling the cracks and forming rims around the quartz grains. The groundmass is composed, principally, of cristobalite, with moderate amounts of tridymite. The tridymite crystals are small but well formed. In isolated instances pseudowollastonite forms the rim around the shattered quartz grain instead of cristobalite. Very little glass appears to be present in the brick. Small amounts of pseudowollastonite are present in the thin section in isolated patches. The brick appears very similar to brick (2) of manufacturer (*a*). The mineralogical composition is given in Table 5.

(3) *Reburned Brick.*—The company remarks concerning the burning of this brick: "It has been subjected to repeated burnings, the number of times we are unable to determine; but we can safely say that the place this brick was taken from is the flash wall in our kiln and these walls stand six to eight burns before they are torn down." The maximum temperature reached in burning was presumably the same as in the burning of the regular brick of this company. The brick appears denser than the regular brick, deeper yellow in color and the groundmass is more vitreous. Only a few remnants of the original quartz grains remain in the phenocrysts. In most cases the quartz of the phenocrysts has been transformed entirely to cristobalite. The groundmass is composed, principally, of well-developed tridymite crystals, with smaller amounts of cristobalite (Fig. 10). Glass and pseudowollastonite are also found in small amounts in the groundmass. The tridymite crystals are considerably larger than those found in the regular brick of this company. The largest tridymite noted is about 0.15 mm long. The mineralogical composition of this brick is given in Table 5.

MANUFACTURER (c)

(1) The ganister rock submitted is grayish colored and possesses the granular sugary appearance of a siliceous sandstone. At the same time it is hard, tough, and nonfriable. Under the

microscope anhedral, rounded quartz grains can be observed cemented together by a siliceous material most of which has crystallized in smaller grains. A small amount is still isotropic. Some sericite and limonite are present between the quartz grains (Fig. 11). The source of this rock is the Homewood sandstone of the Pottsville formation (Upper Carboniferous). The chemical analysis is given in Table 3.

(2) *Regular Brick, One Burn.*—According to information received, the regular brick was burned at a temperature corresponding to Seger cone 16 (about 1460° C). The burning period was about 9 days and the maximum temperature held from 24 to 36 hours. The chemical analysis is given in Table 4. Megascopically the brick is almost white, with a dull luster, and contains a few spots with a yellow color where some fluxing has taken place. The brick is composed, principally, of quartz. The phenocrysts show large, usually unshattered quartz grains surrounded by rims of cristobalite. The groundmass is composed, principally, of shattered quartz grains and cristobalite (Fig. 12). There is no tridymite present. Small amounts of pseudowollastonite are noted with little or no glass. The mineralogical composition is given in Table 5.

MANUFACTURER (d)

(1) *Quartzite.*—This company uses a grayish, vitreous quartzite mined at the southern end of Blair County, Pa. It is probably the Medina quartzite, since this is used by other companies operating in this region. It has been previously described.

(2) *Regular Brick, One Burn.*—From information obtained the practice of this company is a maximum burning temperature of 2800° F (1538° C) maintained for 24 hours, the total duration of a burn being six and one-half 24-hour days. By visual examination the brick consists of dull white phenocrysts and a granular, more or less vitreous, yellowish groundmass. The groundmass is sometimes black where slag spots appear. The predominant constituents of this brick are quartz and cristobalite. The phenocrysts are composed of more or less shattered quartz grains, with cristobalite filling the interstices and cracks and forming rims around the quartz grains and phenocrysts. The groundmass is made up principally of cristobalite, with small amounts of tridymite (Fig. 15). The tridymite crystals are very small. A very small amount of glass surrounds some of the tridymite crystals. Very little pseudowollastonite is present. The chemical

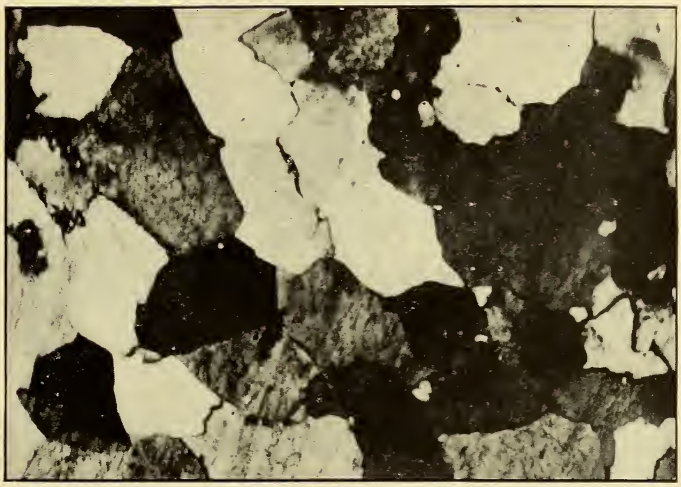

FIG. 9.—*Quartzite used by manufacturer (a) taken with plane polarized light and crossed nicols*

Magnification=40 diameters

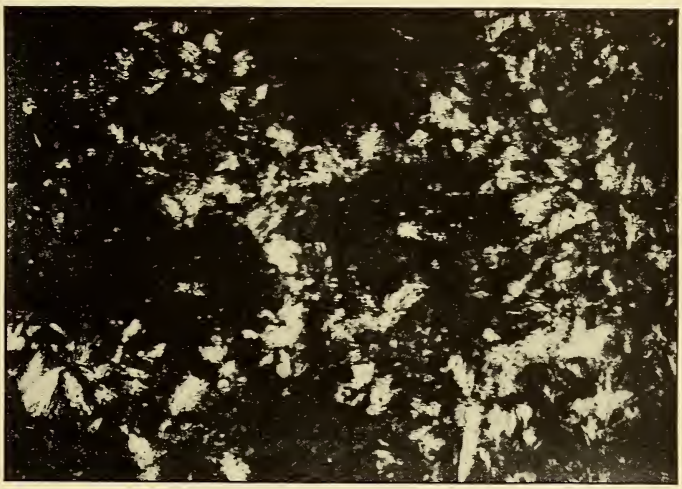

FIG. 10.—*Groundmass of brick (3) of manufacturer (b) as taken with plane polarized light and crossed nicols and showing tridymite and cristobalite*

Magnification=160 diameters

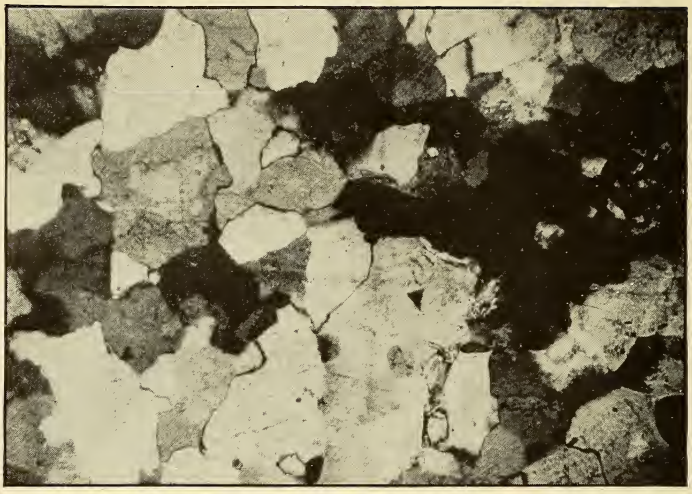

FIG. 11.—*Quartzite used by manufacturer (c), as taken with plane polarized light and crossed nicols*

Magnification=60 diameters

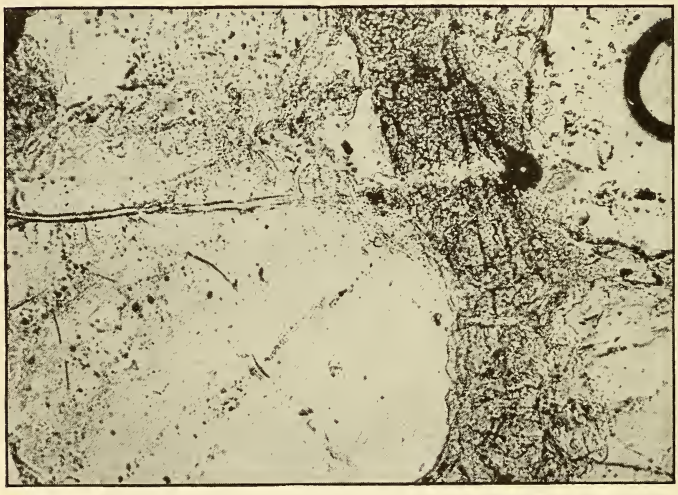

FIG. 12.—*Regular brick of manufacturer (c), showing unshattered quartz phenocrysts and cristobalite rims in ordinary light*

Magnification=160 diameters

analysis of the brick is given in Table 4, and the mineralogical composition in Table 5.

MANUFACTURER (e)

(1) *Quartzite.*—No data are available concerning the geological formation from which the ganister used by this company is quarried, but the location of the quarries indicates that it is probably the Medina quartzite. The material submitted consists of a hard, dense, vitreous quartzite showing limonitic discoloration on weathered surfaces. The chemical analysis is given in Table 3. Microscopically it is identical with known Medina quartzite. The quartz crystals are anhedral to subhedral and the original siliceous bond has entirely crystallized. A small amount of sericite is observed in veinlets running through the specimen.

(2) *Regular Brick, one Burn.*—This brick is apparently well burned and appears hard and tough. The phenocrysts are white and sugary, while the groundmass is yellow in color, granular, and vitreous. Dark-colored slag spots are present. The chemical analysis is given in Table 4. The predominant constituents of the brick are tridymite and cristobalite. Remnants of shattered quartz crystals are sometimes seen in the phenocrysts, but the phenocrysts are usually composed entirely of cristobalite (Figs. 13 and 14). Besides cristobalite, tridymite is the chief constituent of the groundmass. Wedge-shaped twins of tridymite fairly large and often well developed are common. There are certain areas in which the tridymite crystals are much smaller, probably due to the absence of sufficient amounts of flux. A fairly large amount of glass is present in the groundmass. Pseudowollastonite is present only in small amounts. The mineralogical composition is given in Table 5.

(3) *Reburned Brick.*—No data are available concerning the heat treatment of this brick. It appears denser, more vitreous, and less granular than the regular-burn brick. The white phenocrysts have not disappeared, but are still prominent in the yellowish groundmass. The groundmass is a deeper yellow than that of the regular brick. The number of slag spots seem to have increased. Tridymite is present in somewhat greater quantities, and the crystals are larger than in the regular-burn brick. Remnants of shattered quartz grains are sometimes present in the phenocrysts, but in most cases the phenocrysts are completely changed to cristobalite. Glass is noted between and around the tridymite crystals. Pseudowollastonite is present in much larger quantities than in the regular brick. The mineralogical composition is given in Table 5.

2. WISCONSIN-ILLINOIS-INDIANA BRICK

MANUFACTURER (f)

(1) *Quartzite.*—The quartzite used by this company is obtained from the Baraboo (pre-Cambrian) formation of Wisconsin. The sample submitted is a dense, vitreous quartzite with a purplish-red tinge. Under the microscope the quartz crystals are seen to be anhedral to subhedral. Many of the larger grains show undulatory extinction. The original siliceous cement has entirely crystallized either in small quartz crystals or in crystallizing has followed the primary anhedral quartz grains resulting in subhedral crystals which show some tendency toward hexagonal development. Sericite is noted in veinlets (Fig. 16). The chemical analysis is given in Table 3.

(2) *Regular Brick, One Burn.*—According to the information received, "the regular burned brick was under fire for eight and one-half days, reaching a maximum temperature of about 2850° F (1566° C), which was maintained for a period of 24 hours." The brick consists of white to gray phenocrysts, with a sugary appearance and a yellow groundmass. The brick is vitreous and granular and contains a considerable number of slag spots. The chemical analysis is given in Table 4. The phenocrysts are composed of almost unchanged quartz grains, usually more than one to a phenocryst. The phenocrysts are surrounded by rims of cristobalite. The groundmass is principally cristobalite, with considerable amounts of tridymite and a few isolated quartz grains. The tridymite crystals are quite small. A large amount of yellowish-green glass is present, but there is very little pseudowollastonite. The mineralogical composition is given in Table 5.

(3) *Reburned Brick.*—The brick had about three or four burns, the temperatures and duration of each burn being about the same as for the regular brick of this company. The brick is composed principally of tridymite with some cristobalite (Figs. 17 and 18). There is very little quartz present. The quartz of the phenocrysts has been transformed almost entirely to cristobalite, with a few small tridymite crystals present. The groundmass is almost entirely tridymite. The tridymite crystals in the groundmass are much larger than those in the phenocrysts, the largest being about 0.2 mm long. There are comparatively large amounts of yellow glass present in the groundmass, in which the tridymite crystals are apparently embedded. The tridymite crystals in the groundmass are usually large, well-developed twins. Very little pseudowollastonite is present. The mineralogical composition is given in Table 5.

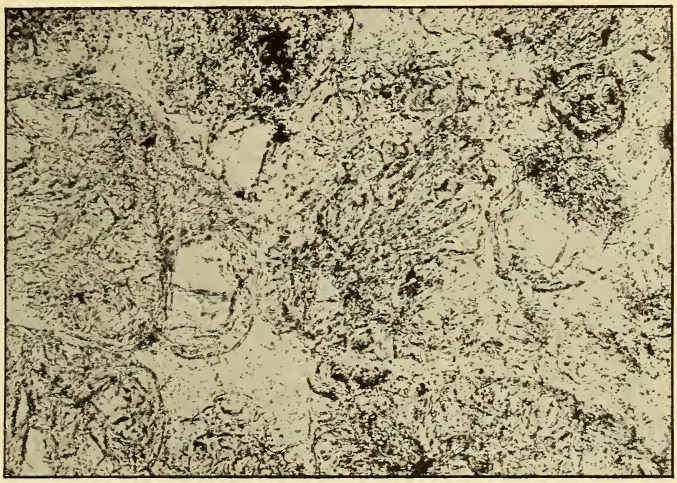

FIG. 13.—*Regular brick of manufacturer (e) taken in ordinary light*

Magnification= 160 diameters

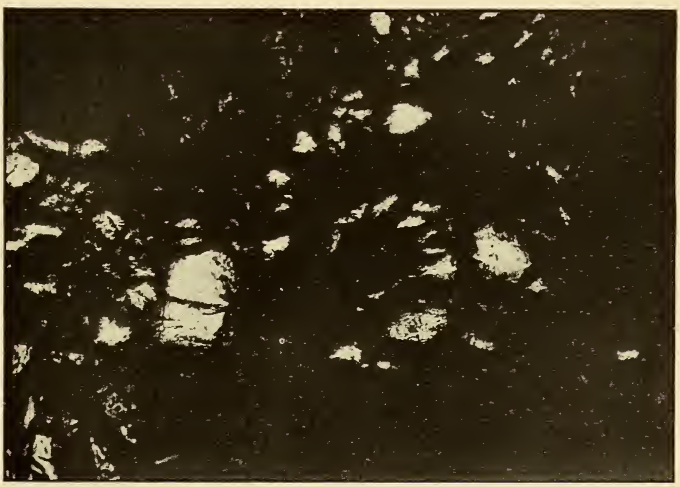

FIG. 14.—*Same as Fig. 13, but taken with plane polarized light and crossed nicols*

Note the small amount of doubly refracting quartz in the phenocrysts. The small crystals are mainly tridymite. The black area is cristobalite. Magnification= 160 diameters

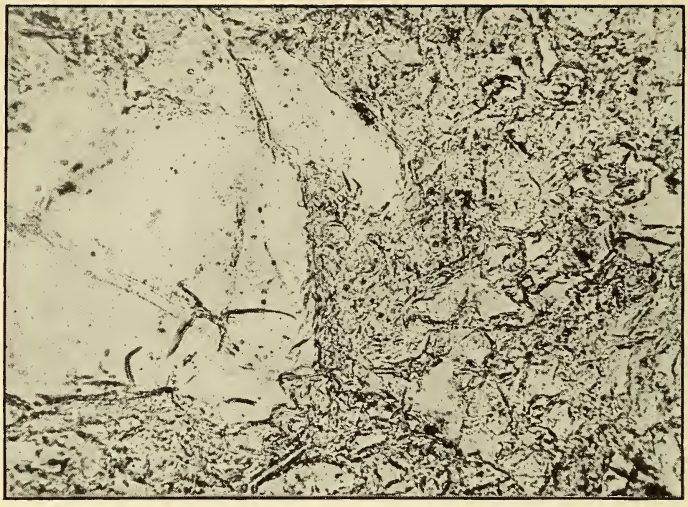

FIG. 15.—*Regular brick of manufacturer (d) taken in ordinary light*

Magnification= 160 diameters

FIG. 16.—*Quartzite used by manufacturer (f) taken with plane polarized light and crossed nicols*

A veinlet of sericite is seen running across the center of the field. Magnification= 40 diameters

MANUFACTURER (g)

(1) *Chert.*—The chert, which is the raw material from which the brick of this company are made, is a hard rock of vitreous luster, much finer grained than the usual quartzites. Microscopically it appears to be made up of small aggregates of chalcedony, minute quartz crystals, and amorphous siliceous material.[17] The chemical analysis is given in Table 3.

(2) *Regular Brick.*—Information as to exact burning conditions is not available, but the brick probably had about the same burn as the ordinary, regular-burn, silica brick. The brick has a light-yellow color. Phenocrysts are numerous. Their luster is usually vitreous, although sometimes they have a flinty appearance. The chemical analysis is given in Table 4. Microscopic examination shows an unusual condition. The brick is composed almost entirely of small tridymite crystals. The phenocrysts are distinguished from the groundmass only by the relative size of the tridymite crystals, the crystals in the phenocrysts being much smaller than those in the groundmass. There is very little glass or pseudowollastonite present. The mineralogical composition is given in Table 5. The almost complete inversion to tridymite is probably due to the fine-grained condition of the chert, chalcedony being one of its principal constituents.

MANUFACTURER (h)

(1) *Quartzite.*—The quartzite used is from the Baraboo formation and is very similar, both megascopically and microscopically, to that used by manufacturer (*f*). The chemical analysis is given in Table 3.

(2) *Regular Brick, One Burn.*—The burning conditions of the regular brick are practically identical with those of the regular brick of manufacturer (*a*). The brick consists of dull-white phenocrysts and a yellow, more or less vitreous groundmass which contains many gray to black slag spots. Microscopically the phenocrysts consist of shattered quartz grains with the cracks showing some inversion to cristobalite. The phenocrysts are surrounded by the typical cristobalite rims. Cristobalite is the chief constituent of the groundmass, although some quartz is also present. Tridymite is found in only small quantities. A very small amount of

[17] The analyses of the chert, the chert brick, and the German brick (Stella Werke * * *) are taken from a manuscript of a paper on silica brick by D. W. Ross.

glass is present and but little, if any, pseudowollastonite. The chemical analysis is given in Table 4, and the mineralogical composition in Table 5.

3. ALABAMA BRICK

MANUFACTURER (i)

(1) *Quartzite.*—The quartzite used by this company is probably of Lower Cambrian age. The color of the quartzite is gray, but somewhat darker than the Medina quartzite. Microscopically the material resembles a great deal the Baraboo quartzite, although here the fine-grained, quartzitic cementing material occurs in smaller amounts than in the Baraboo quartzite. Sericite is not so common in this quartzite as in the Baraboo (Fig. 19). The chemical analysis is given in Table 3.

(2) *Regular Brick, one Burn.*—The brick is yellowish in color and contains comparatively few phenocrysts. The flux appears to have thoroughly permeated the granular groundmass, which has a decided vitreous lustre. The larger phenocrysts consist of aggregates of quartz crystals separated from each other by interstitial cristobalite. The smaller phenocrysts consist of cristobalite which surrounds corroded remnants of quartz grains. The groundmass consists of cristobalite, tridymite, quartz, glass, and pseudowollastonite. Tridymite crystals are small, the wedge-shaped twins being the most common forms. The chemical analysis is given in Table 4 and the mineralogical composition in in Table 5.

4. MONTANA BRICK

MANUFACTURER (j)

(1) *Quartzite.*—The quartzite used by this company is quarried from the Quadrant formation of Upper Carboniferous age. It is a fine-grained, dense, vitreous quartzite with a conchoidal to uneven fracture. There is a very little of the fine-grained siliceous cementing material present, but there is considerable sericite. The chemical analysis is given in Table 3.

(2) *Brick No. 1.*—This is a dry-pressed brick burned at a maximum temperature of cone 14 (about 1410° C), the entire burning process requiring about three weeks. The brick has a yellow color and small, sugary phenocrysts. Microscopically the brick shows an unusual condition. The phenocrysts are often composed wholly of unaltered and unshattered quartz grains, although the quartz grains sometimes show cristobalite rims. The groundmass is composed almost entirely of quartz, cristobalite, and pseudo-

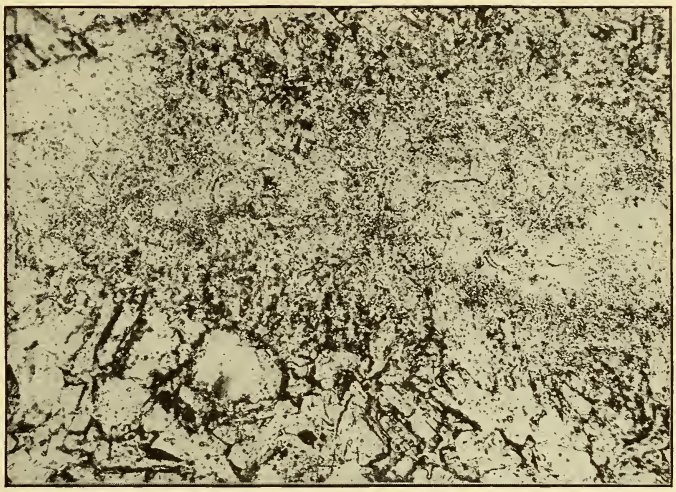

FIG. 17.—*Reburned brick (3) of manufacturer (f) taken in ordinary light*

No large quartz grains are present. Magnification=160 diameters

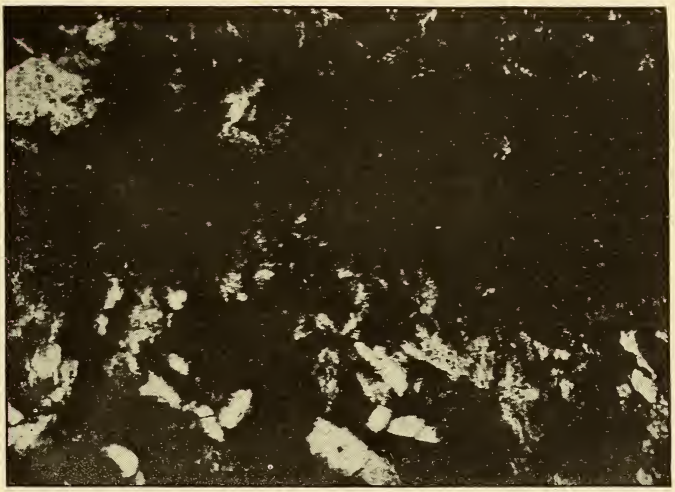

FIG. 18.—*Same as Fig. 17, but taken with plane polarized light and crossed nicols*

Nearly all the doubly refracting grains are tridymite; the dark portions are cristobalite. Magnification=160 diameters

FIG. 19.—*Quartzite used by manufacturer (i) taken with plane polarized light and crossed nicols*

Magnification=60 diameters

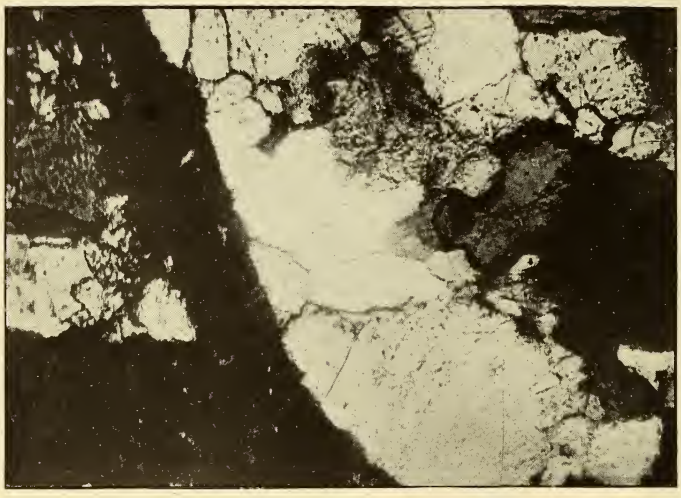

FIG. 20.—*Regular brick No. 1 of manufacturer (j) taken with plane polarized light and crossed nicols*

Note the large, almost unaltered phenocryst of the original quartzite. Magnification=160 diameters

wollastonite (Fig. 20). The brick is notable for the large amount of pseudowollastonite which it contains. There is no glass or tridymite present. Apparently the phenocrysts make up about as much of the volume of the brick as does the groundmass. The chemical analysis is given in Table 4 and the mineralogical composition in Table 5.

(3) *Brick No. 2.*—This is a special brick; hand molded, re-pressed, and burned in a continuous railroad-tunnel kiln at a temperature of cone 14 (about 1410° C). It was completely heated up, burned, and cooled in 78 hours. Megascopically the brick differs considerably in appearance from the preceding one; the fracture surface is rougher and the phenocrysts are more numerous and considerably larger. The groundmass, because of the larger amount of flux associated with it, is more deeply colored. Although there is as much or more quartz present than in the preceding brick, the phenocrysts show much more shattering. Quartz and cristobalite are the chief constituents of the groundmass. There is no tridymite present, but considerable pseudowollastonite. Glass is apparently absent. The chemical analysis is given in Table 4 and the mineralogical composition in Table 5.

(4) *Brick No. 3.*—This brick is a sample of the regular burn of this company; hand molded, re-pressed, and burned in the same manner as brick No. 1. Quartz is by far the most abundant constituent both of the phenocrysts and of the groundmass. The phenocrysts consist almost wholly of unaltered and unshattered quartz grains surrounded by crystobalite rims. There is considerable pseudowollastonite present, but not as much, apparently, as in brick No. 1. There is no tridymite or glass present. The chemical analysis is given in Table 4 and the mineralogical composition in Table 5.

The foregoing brick are interesting because of the large amount of quartz remaining and more particularly because of the unaltered and unshattered quartz grains in the phenocrysts. Two factors contribute toward this condition: First, the low-burning temperature tends to lessen the amount of quartz which inverts to cristobalite; secondly, it will be noticed that the bricks which show no shattering have been subjected to a long burn, lasting three weeks. This would allow slow elevation of the temperature, and thus reduce strains set up in the brick by differences of temperatures within and without. More shattering of the grains has occurred in the brick of short burn.

5. UNUSUAL BRICKS AND TEST SPECIMENS

BUREAU OF STANDARDS CUBES (k)

A number of 2-inch cubes were made up from a standard commercial silica-brick mix and burned at different temperatures. The quartzite used in the mix was from the Tyrone district, Pennsylvania.[18] All the cubes were first burned to about 1150° C in three days, after which the cubes were burned to successively higher temperatures each time, one cube being removed at each burn for microscopic analysis. At each burn about 18 hours were required for heating to 800° and about 6 hours for heating from 800° to the desired temperature. The mineralogical composition of all cubes is given in Table 5.

1. *1200° Cube.*—This cube consists entirely of quartz. Cristobalite and tridymite are absent. The cube resembles the original quartzite to a great extent, the quartz grains showing no shattering.

2. *1250° Cube.*—This cube resembles the 1200° cube to a great extent, except that the quartz grains show more shattering. The beginning of the formation of cristobalite is noted in the groundmass. There are no evidences of the presence of tridymite, pseudowollastonite, or glass.

3. *1300° Cube.*—In this cube the grains are more thoroughly shattered. The development of cristobalite is noted in the groundmass and in the cracks in the quartz grains. Tridymite, pseudowollastonite, and glass are absent.

4. *1350° Cube.*—The only minerals present are quartz and cristobalite. The quartz grains are thoroughly shattered, crystobalite filling the cracks and surrounding the grains.

5. *1400° Cube.*—This cube resembles the 1350° cube to a great extent. A very small amount of pseudowollastonite is apparent. Tridymite and glass are absent.

6. *1450° Cube.*—Cristobalite is the principal constituent of this cube. Tridymite crystals make their appearance for the first time. The crystals are very small. A small amount of pseudowollastonite is present.

7. *1500° Cube.*—This cube shows a much greater quantity of tridymite than the 1450° cube. The tridymite crystals even appear in some of the phenocrysts. Nearly all of the quartz has been transformed to cristobalite. A very small amount of pseudowollastonite is present.

[18] Information as to raw material and burning conditions of these cubes was taken from a manuscript of a paper on silica brick by D. W. Ross.

8. *1500° Cube, Burned Three Times.*—Quartz is practically absent in this cube. Tridymite and cristobalite are the principal constituents, with cristobalite predominating. The tridymite crystals are much larger and more perfectly developed than in the other cubes. Glass and pseudowollastonite are present in small quantities.

In all of these test cubes it is much harder to distinguish the phenocrysts from the groundmass than it is in the ordinary commercial silica brick.

GERMAN BRICK (l)

This brick has the brand Stella Werke * * *. Information as to the quartzite used as raw material and the burning conditions of the brick is not available. The brick has a yellowish-brown color. The phenocrysts are large and rather numerous, most of them with a white color, although some have a dark and flinty appearance. The brick is notable for the large number of black slag spots that it contains. The phenocrysts are composed of numerous small, angular, quartz grains, which show very little shattering, each phenocryst usually containing more than one quartz grain. The quartz grains are of much smaller size than those usually found in bricks of American manufacture. The cristobalite surrounds the quartz grains and forms rims around the phenocrysts. The groundmass is principally cristobalite with a subordinate amount of tridymite. The tridymite crystals are very small. There is very little glass or pseudowollastonite present. The chemical analysis is given in Table 4 and the mineralogical composition in Table 5.

COKE-OVEN BRICKS (m)

This brick was taken from a Koppers by-product coke oven, after having been in use for about nine years [19]. It was made from Baraboo quartzite. The brick was in place 6 inches above the floor of the coking chamber, 20 feet from the pusher end, with one of its sides exposed to the coke and the other to the flue gases. The maximum temperature on the heating side of the brick probably reached about 1535° C, while the average temperature was about 1315° C. On the coke side of the brick the average temperature was about 1095° C. Since temperatures near the average temperatures just given are sustained in coke ovens for long periods of time, they probably have more influence upon the end products of the inversion in the brick than the highest tem-

[19] Information as to raw material and burning conditions of the coke brick was taken from the unpublished manuscript by D. W. Ross.

peratures reached. The brick is particularly hard and tough and shows a very low porosity. It has a more vitreous luster than the ordinary commercial brick. Thin sections were made from three parts of the brick—one from the side next to the flue, one from the central portion, and one from the side next to the coke. Microanalyses were also made from these three parts.

(1) *Section from Flue Side of Brick.*—This portion of the brick is very light colored, almost white, and the phenocrysts are not easily distinguishable from the groundmass. The section consists almost entirely of tridymite crystals. The phenocrysts can sometimes be recognized in thin section by the smaller size of the tridymite crystals in them. There is no pseudowollastonite, and the quantity of glass present is not large. The largest tridymite crystal seen in this section measured about 0.6 mm in length. The mineralogical composition is given in Table 5.

(2) *Section from Central Part of Brick.*—In this part of the brick the color grades from yellow near the coke side to reddish brown near the flue side. Here the phenocrysts are more easily seen than in the section from the flue side. The quartz grains are scarce and always possess corroded and rounded edges. In some cases the phenocrysts consist entirely of cristobalite and minute tridymite crystals. In the groundmass tridymite is predominant, the crystals having a larger size than those of the phenocrysts. They are larger also than the tridymite crystals in the groundmass of the coke side of the brick. The quartz grains in the phenocrysts are surrounded by cristobalite rims. There is no noticeable glass or pseudowollastonite present. The mineralogical composition is given in Table 5.

(3) *Section from Coke Side of Brick.*—The groundmass of the coke side of the brick has a dark color, while the phenocrysts are large, sugary, and white. The phenocrysts are made up of quartz and cristobalite. Where a single quartz grain occupies a phenocryst its edges are well rounded and the grain is surrounded by a very distinct rim of cristobalite. The tridymite crystals are usually small, wedge-shaped twins. There is no noticeable glass or pseudowollastonite. The mineralogical composition is given in Table. 5.

VI. THE STRUCTURE OF SILICA BRICK

In almost every case the brick is found to have a porphyritic-like structure made up of phenocrysts and groundmass. This structure is not due to any chemical or physical action that takes

place during the heating or cooling of the brick, but is caused entirely by the method of grinding the raw material. The phenocrysts are the coarsely ground pieces of raw material, while the groundmass is made up of the finely ground material and the rock flour.

By microscopic examination of thin sections it is found that the inversion begins first in the groundmass of the brick. Here cristobalite begins to form. The material which is broken up in the phenocrysts by the shattering due to expansion on heating is then transformed to cristobalite, and rims of cristobalite form around the phenocrysts very similar in appearance to the reaction rims seen around minerals in natural rocks. After longer heating the tridymite begins to appear in the groundmass. At first the crystals are exceedingly small and somewhat poorly developed. With successive reburnings they increase in size. Tridymite usually forms simple, wedge-shaped and more complicated interpenetration twins. In reburned brick the quartz phenocrysts are sometimes seen to be entirely transformed to cristobalite, and sometimes even tridymite crystallites begin to appear in the phenocrysts.

The presence of tridymite in bricks which have had maximum burning temperatures above the tridymite-cristobalite inversion point seems difficult of explanation. It is probable in cases where the brick did reach these high temperatures that during the greater portion of the heating period its temperature was well below the inversion point. It is probable, too, that while the temperature recorded in the kiln was above 1470° C (the tridymite-cristobalite inversion point) the temperature below the surface of the brick was not nearly so high. There is also a third possibility that the temperatures as indicated by Seger cones in the body of the kiln under the conditions were higher than the actual temperatures.

VII. THE ACTION OF THE LIME

The greater the amount of flux in the brick the more quickly will the silica be changed into the end product of inversion. It has been found, however, that the addition of lime above 6 or 8 per cent greatly depresses the softening temperature of the brick.[20]

Although the addition of lime hastens the inversions of silica and thus increases the strength of the brick, the lime itself and the compounds which it forms seem to play but a small part in the

[20] Taken from unpublished manuscript by D. W. Rose.

cementing of the finished brick. Most of the bonding action of the brick seems to come from the interlocking of the cristobalite and tridymite crystals. The glass which sometimes appears to form a matrix for the tridymite crystals may also aid in the bonding of the bricks. The coke-oven brick (*m*), however, which apparently contained little glass, was exceedingly hard and tough. The cross-breaking strength of a brick may be the measure of the strength of its bond.

VIII. THE CAUSES OF PERMANENT EXPANSION

The important effect in silica brick of the inversion of quartz to other silica minerals is the effect on its permanent expansion. The complete transformation of quartz to cristobalite gives a volume increase of 13.6 per cent; quartz to tridymite, 16.8 per cent. The permanent expansion of silica brick after the usual commercial burn amounts to about 10 or 11 per cent by volume.[21]

If most of the permanent expansion is not taken out during the burning the brick will expand after it has been put into use, causing buckling of the furnace walls. A brick in which all the silica present had been transformed into tridymite would have reached the limit of its permanent expansion. From the standpoint of permanent expansion alone, therefore, a brick composed wholly of tridymite would be the perfect silica brick.

Not only has the transformation of quartz into cristobalite and tridymite great influence on the permanent expansion of silica brick, but it also has a noticeable effect on the qualities of the brick, such as its crushing strength, cross-breaking strength, and spalling tendency.

McDowell [21] concluded, after testing a number of bricks having varying burns, that brick of regular grind increase in strength (both compressive and cross-breaking) on each burn up to the third. His spalling tests showed that the spalling tendency diminishes on repeated burning.

McDowell gives the following reasons for the desirability of having a large proportion of tridymite in silica brick, providing the brick are not to be heated continuously above 1470° C:

(*a*) Tridymite has the least thermal or temporary expansion of the three silica minerals.

(*b*) Tridymite has the greatest specific volume of the three minerals, and can not show any permanent expansion after repeated burning below its melting point.

[21] McDowell: A Study of the Silica Refractories, Bull. 119, Amer. Inst. of Min. Eng., November, 1916.

(*c*) A tridymite brick could probably be subjected to fairly rapid changes of temperature with little danger of cracking.

It seems to be generally conceded, however, that the length of time required in burning would make a commercial all-tridymite brick economically impossible.

IX. SUMMARY

Petrographic microscopic examinations of commercial silica brick and those which have received repeated burnings by use in kilns show three main constituents—quartz, cristobalite, and tridymite. In addition, small amounts of pseudowollastonite ($\alpha - CaO.SiO_2$) and glass are present. Long burning at slightly less than 1470° C causes the formation of a large percentage of tridymite. Cristobalite is characteristic of higher-burned brick. The quartz first inverts to cristobalite in the fine-grained groundmass and along cracks caused by shattering on heating, and later to tridymite if the temperature does not exceed 1470° C. The lime added in grinding aids more as a flux than as a bond. The interlocking of the quartz, cristobalite, and tridymite crystals provides most of the cementing action in the burned product.

The petrographic microscopic examination of silica brick makes it possible to obtain information concerning their quality, particularly as to whether they are subject to further permanent expansion. This expansion, being due to the inversion of quartz to tridymite and cristobalite, becomes a dangerous possibility when enough quartz has not been transformed into the other high-temperature forms of silica during the first burning. Quartz should first be looked for in examining silica brick with the microscope. Tridymite and cristobalite may also be noted, but these are not as important in this connection. The estimation of the amounts is preferably made by the method used in this paper. A fair accuracy is obtainable in this way. No definite limit of the amount of quartz allowable can be stated. It should not, however, be large. A low-quartz brick should show very little further permanent expansion.

Starting with a standard commercial mix, two factors—time and temperature—govern the constitution of the resulting brick. The microanalyses of various bricks show that the longer the brick is burned at high temperatures (below 1470°) the greater will be the amount of tridymite present. Given time enough, this would result in an all-tridymite brick, which would be highly

desirable from the standpoint of permanent expansion. The cost of production prevents this in commercial practice. A shorter burn at a higher temperature results in the transformation of the quartz to a large extent into cristobalite and some tridymite, which is satisfactory and commercially practicable.

This investigation has verified the prediction of Fenner that, with a comparatively small amount of flux, quartz inverts to cristobalite, then to tridymite at temperatures where cristobalite is the unstable, and tridymite is the stable modification. In the case of every brick examined cristobalite was the first inversion product to form whether the burning conditions had been such as to promote much or little inversion. Moreover, the final inversion product, reached after many reburnings to the temperature range where it was the stable modification, resulted invariably in the formation of tridymite. The order of inversion here is seen to follow Ostwald's Law of Successive Reactions quoted in the introduction to this paper.

X. ACKNOWLEDGMENTS

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TABLE 3.—Chemical Analyses of Silica Rocks Used in Making Silica Brick

	a1 Medina quartzite	b1 Medina quartzite	c1 Home-wood sand-stone	d1 Medina quartzite
SiO_2	97.84	96.78	95.85	98.23
Fe_2O_3	.30	.53	.42	.38
Al_2O_3	1.29	2.35	3.35	1.43
CaO	.02	.04	.03	.05
MgO	.....	.....	.....	.....
	99.45	99.70	99.65	100.09

	e1 Medina quartzite	f1 Baraboo quartzite	j1 Quad-rant quartzite	h1 Wiscon-sin quartzite
SiO_2	97.96	96.90	97.27	98.26
Fe_2O_3	.55	.93	.53	.22
Al_2O_3	1.63	1.84	1.84	1.64
CaO	.02	.03	.07	Trace
MgO	.....	.....	.....	.....
	100.16	99.70	99.71	100.12

	i1 Alabama quartzite	g1 Indiana chert [a]
SiO_2	97.25	96.67
Fe_2O_3	.63	.48
Al_2O_3	1.58	1.59
CaO	.10	.07
MgO	.08	.....
Ignition	.34	1.26
K_2O	.....	.15
Na_2O	.....	.05
	99.98	100.08

[a] The analysis of Indiana chert is taken from a manuscript of a paper on silica brick by D. W. Ross.

TABLE 4.—Chemical Analyses of Silica Brick

	a2	b2	c2	d2	e2	f2	h2	i2	j2	i3	l4
SiO_2	96.78	96.68	96.22	97.41	97.01	96.66	95.04	96.62	95.84	97.69	95.90
Fe_2O_3	.51	.82	.44	.53	.40	.88	1.61	.80	.88	.46	.70
Al_2O_3	1.38	1.22	1.47	.81	1.29	1.22	1.12	1.09	1.47	.78	1.72
CaO	1.65	1.48	2.09	1.48	1.60	1.56	1.87	1.84	2.07	1.41	2.06
	100.32	100.20	100.22	100.23	100.30	100.32	99.64	100.35	100.26	100.34	100.38

	g2 (chert brick) [a]	1 (German brick) [a]
SiO_2	95.60	94.20
Fe_2O_3	.61	1.62
Al_2O_3	1.80	1.60
CaO	2.01	2.24
MgO	.....	.09
K_2O	.16	.....
Na_2O	.06	.....
Ignition	.12	.....
	100.36	99.75

[a] The analyses of the chert brick and the German brick were taken from a manuscript of an unpublished paper on silica brick by D. W. Ross.

TABLE 5.—Mineralogical Composition of Silica Brick

	Specimen	Quartz and silicates	Tridymite	Cristobalite
a2	Regular brick, 1 burn	13.0	15	72.0
a3	Special brick, 6 burns	9.0	78	13.0
a4	Brick used in magnesite kiln	10.0	86	4.0
a5	Brick used in crown of clay kiln	13.0	86	1.0
b2	Regular brick, 1 burn	22.0	7	71.0
b3	Reburned brick	12.0	71	17.0
c2	Regular brick, 1 burn	75.0	None	25.0
d2	Regular brick, 1 burn	43.0	Trace	57.0.
e2	Regular brick, 1 burn	9.0	36	55.0
e3	Reburned brick	14.0	60	26.0
f2	Regular brick, 1 burn	40.0	8	52.0
f3	Reburned brick	8.0	75	17.0
g2	Chert brick	5.0	83	12.0
h2	Regular brick, 1 burn	44.0	4	52.0
i2	Regular brick, 1 burn	14.0	13	73.0
j2	Brick No. 1	61.0	None	39.0
j3	Brick No. 2	72.0	None	28.0
j4	Brick No. 3	70.0	None	30.0
k1	Bureau of Standards 1200° cube	100.0	None	None
k2	Bureau of Standards 1250° cube	92.0	None	8.0
k3	Bureau of Standards 1300° cube	72.5	None	27.5
k4	Bureau of Standards 1350° cube	48.0	None	52.0
k5	Bureau of Standards 1400° cube	30.0	None	70.0
k6	Bureau of Standards 1450° cube	16.0	(a)	83.0
k7	Bureau of Standards 1500° cube	11.0	10	79.0
k8	Bureau of Standards 1500° cube, 3 burns	6.0	24	70.0
1	German brick (Stella Werke * * *)	20.0	2	78.0
m–A	Coke oven brick, flue side	8.0	89	3.0
m–B	Coke oven brick, center	20.0	67	13.0
m–C	Coke oven brick, coke side	31.0	45	24.0

[a] Less than 1 per cent.

WASHINGTON, *October 11, 1918.*